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(54) **Liquid automatic dishwashing composition.**

(57) Specific ether carboxylate molecules which are both hypochlorite resistant and biodegradable are described for use in a non-phosphate based automatic dishwashing liquid composition. The ether carboxylate molecules are oxydisuccinates.

EP 0 550 087 A1

FIELD OF THE INVENTION

The present invention is concerned with organic detergent builders which are both hypochlorite resistant and biodegradable for use in automatic dishwashing detergent liquids. Specifically, select ether carboxylates are used to prepare zero- or low-phosphate based detergent compositions.

BACKGROUND OF THE INVENTION

Liquid detergents for automatic dishwashers have been commercialized since the mid-1980s and have overcome many problems encountered with powder detergents. In particular powder detergents lose solubility on aging, cake in the dispenser cup and generate fine particles upon dispensing.

Efforts have also been made since the late 1960s to replace the high levels of phosphate builders in both powder and liquid detergent products with non-phosphate ingredients which fulfill builder functions without causing environmental damage. Builders in automatic dishwashing products function to provide alkalinity, sequester hardness ions and disperse soils so as to prevent redeposition on clean dishware surfaces.

Unfortunately, many organic or environmentally friendly builders are hypochlorite sensitive and thus unstable in the presence of a chlorine bleaching agent, especially in liquid detergent compositions.

In U.S. 4,933,101 (Procter & Gamble) numerous polycarboxylates are disclosed as suitable for combination with a chlorine source to prepare detergent compositions. However, this patent exemplifies only powdered compositions and states that builders such as citrate have particularly good dishwashing performance. Citrate is not, however, stable in the presence of free hypochlorite and breaks down in a liquid detergent composition.

Ether carboxylate compounds are disclosed in U.S. 4,689,167 (P&G) and 4,687,592 as useful detergent builders. The patents, however, are silent on the hypochlorite resistance of these organic builders in liquid detergent compositions, as well as their biodegradability. Surprisingly, particular ether carboxylates have been discovered to both possess chlorine bleach stability while being readily biodegradable and useful for providing a zero- or low-phosphate liquid detergent composition. Ether carboxylates possess ether linkages which resemble the ether linkages present in ethoxylated nonionic surfactants. Ethoxylated nonionic surfactants, such as the Neodol® series owned by Shell Inc., are notoriously unstable in the presence of chlorine bleach.

It has also been observed that ether carboxylates, such as ethylene glycol disuccinate (EGDS) and propylene glycol disuccinate (PGDS), are chlorine stable but are not biodegradable. The present invention not only pertains to particular ether carboxylate molecules which possess surprisingly good chlorine bleach resistance, even at high temperatures, but which are also readily biodegradable.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an automatic dishwashing liquid composition which includes a non-phosphate based builder which is not only readily biodegradable but is surprisingly chlorine bleach resistant.

The object of the present invention is accomplished by providing an automatic dishwashing liquid composition comprising about 3 to about 30% by weight of an ether carboxylate builder selected from a group of compounds known as oxydisuccinates;

a chlorine donor source providing from about 0.2 to about 1.5% available chlorine; about 0.1 to about 6% of a thickening agent; about 3 to about 30% of an inorganic builder; and optionally about 0.5 to about 15% of an anti-scalant agent and about 0.5 to about 4.0% of a low foaming surfactant.

Other optional ingredients such as colorants, dyes, pigments, perfumes anti-tarnish agents, soil suspending agents, hydrotropes and mixtures thereof are also included.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTSEther Carboxylate Builders

The aqueous compositions of the invention contain from about 3 to about 30%, preferably from about 5 to about 20% of an ether carboxylate compound or mixtures thereof selected from compounds known as

oxydisuccinates.

A preferred oxydisuccinate within the scope of the invention includes 2,2'-oxodisuccinate.

The oxydisuccinates of the invention are made by any of the conventional means known in the art.

5 Modified SCAS Test

A semi-continuous activated sludge test (SCAS) for determining the biodegradability of nonionic, linear detergent components was devised by the American Society for Testing and Materials (ASTM) D 2667, p 388-389. This test modified to determine the biodegradability of organic test materials, which at the
10 concentration used in the test:

- (1) are soluble in water (at least 20 mg dissolved organic carbon/liter);
- (2) have negligible vapor pressure;
- (3) are not inhibitory to bacteria;
- (4) do not significantly adsorb on glass surfaces; and
- 15 (5) are not lost by foaming from the test solution.

Therefore, the "modified SCAS test" has been found suitable by the Organization for Economic Cooperation and Development (OECD) for determining the inherent biodegradability of organic chemicals under aerobic conditions and is disclosed in the OECD Guideline for Testing of Biodegradability Chemicals, Test 302A (May 12, 1981), herein incorporated by reference.

20 Test chemicals giving a result of greater than 70 percent loss of degradation of carbon (DOC) within 28 days in this test are regarded as biodegradable. The use of a compound specific analytical technique on ¹⁴C-labelled test substance is another measure of biodegradability.

The modified SCAS test method is an adaptation of the Soap and Detergent Association semi-continuous activated sludge (SCAS) procedure for assessing the primary biodegradation of alkyl benzene
25 sulphonate. The method involves exposure of the chemical to relatively high concentrations of micro-organisms over a long time period (possibly several months). The viability of the micro-organisms is maintained over this period by daily addition of a settled sewage feed.

Because of the long detention period (36 hours) and the intermittent addition of nutrients the test does not simulate those conditions experienced in a sewage treatment plant. The results obtained with the test
30 substance indicate that it has a high biodegradation potential, and for this reason it is most useful as a test of inherent biodegradability.

Since the conditions provided by the test are highly favorable to the selection and/or adaptation of microorganisms capable of degrading the test compound, the procedure may also be used to produce acclimatized inocula for use in other tests. The test is applicable to water soluble, non-volatile, organic
35 chemicals that are not inhibitory to bacteria at the test concentration.

Methodology

Activated sludge from a sewage treatment plant is placed in an aeration (SCAS) unit. The test
40 compound and settled domestic sewage are added, and the mixture is aerated for 23 hours. The aeration is then stopped, the sludge allowed to settle and the supernatant liquor is removed. The sludge remaining in the aeration chamber is then mixed with a further aliquot of test compound and sewage and the cycle is repeated.

Biodegradation is established by determination of the dissolved organic carbon content of the super-
45 natant liquor. This value is compared with that found for the liquor obtained from a control tube dosed with settled sewage only.

DESCRIPTION OF THE TEST PROCEDURE

50 Preparations

The aeration units are cleaned and fixed in a suitable support. The air inlet tubes are connected to the supply manifold. A small laboratory scale air compressor is used to aerate the units, and the air is presaturated with water to reduce evaporation losses from the units.

55 A sample of mixed liquor from an activated sludge plant treating predominantly domestic sewage is obtained. Approximately 150 ml of the mixed liquor are required for each aeration unit.

The organic carbon analyzer is calibrated using potassium hydrogen phthalate.

Stock solutions of the test compounds are prepared: the concentration normally required is 400 mg/litre as organic carbon which gives a test compound concentration of 20 mg/litre carbon at the start of each aeration cycle if no biodegradation is occurring.

The organic carbon content of the stock solutions is measured.

Test conditions

A high concentration of aerobic micro-organisms is used, and the effective detention period is 36 hours. The carbonaceous material in the sewage feed is oxidized extensively within 8 hours of the start of each aeration cycle. Thereafter, the sludge respire endogenously for the remainder of the aeration period, during which time the only available substrate is the test compound unless this is also readily metabolized. These features, combined with daily reinoculation of the test when domestic sewage is used as the medium, provide highly favorable conditions for both acclimatization and biodegradation.

Performance of the Test

A sample of mixed liquor from a suitable activated sludge plant is obtained and aerated during transportation to the laboratory. Each aeration unit is filled with 150 ml of mixed liquor and the aeration is started. After 23 hours, aeration is stopped, and the sludge is allowed to settle for 45 minutes. The tap is opened and 100 ml of the supernatant liquor withdrawn. A sample of settled domestic sewage is obtained immediately before use, and 100 ml are added to the sludge remaining in each aeration unit. Aeration is started anew. At this stage no test materials are added, and the units are fed daily with domestic sewage only until a clear supernatant liquor is obtained on settling. This usually takes up to two weeks, by which time the dissolved organic carbon in the supernatant liquor at the end of each aeration cycle should be less than 12 mg/litre.

At the end of this period the individual settled sludges are mixed, and 50 ml of the resulting composite sludge are added to each unit.

100 ml of settled sewage are added to the control units and 95 ml plus 5 ml of the appropriate test compound stock solution (400 mg/l) to the test units. Aeration is started again and continued for 23 hours. The sludge is then allowed to settle for 45 minutes and the supernatant drawn off and analyzed for dissolved organic carbon content.

The above fill and draw procedure is repeated daily throughout the test.

Before settling it may be necessary to clean the walls of the units to prevent the accumulation of solids above the level of the liquid. A separate scraper or brush is used for each unit to prevent cross contamination.

Ideally, the dissolved organic carbon in the supernatant liquors is determined daily, although less frequent analysis is permissible. Before analysis the liquors are filtered through washed 0.45 µm membrane filters and centrifuged. Temperature of the sample must not exceed 40 °C while it is in the centrifuge.

The length of the test for compounds, showing little or no biodegradation is indeterminate, but experience suggests that this should be at least 12 weeks.

Treatment of the Results

The dissolved organic carbon results in the supernatant liquors of the test units and the control units are plotted against time. As biodegradation is achieved the level found in the test will approach that found in the control. Once the difference between the two levels is found to be constant over 3 consecutive measurements, 3 further measurements are made and the percentage biodegradation of the test compound is calculated by the following equation:

$$\% \text{ biodegradation} = \frac{100 [O_T - (O_t - O_c)]}{O_T}$$

where

O_T = concentration of test compound as organic carbon added to the settled sewage at the start of the

aeration period.

O_t = concentration of dissolved organic carbon found in the supernatant liquor of the test at the end of the aeration period.

O_c = concentration of dissolved organic carbon found in the supernatant liquor of the control.

5 The level of biodegradation is therefore the percentage elimination of organic carbon.

If from the outset there is no difference between the control and the test, or the difference between the two remains constant at a level less than would be expected if no degradation had taken place, further tests are necessary to distinguish between biodegradation and adsorption. This may be done by using the supernatant liquors as a source of inoculum for tests such as the Sturm or the Closed Bottle Tests (OECD
10 Test Guidelines 301 B and 301 D).

Bleaches

A wide variety of bleaching agents may be employed for use with these automatic detergent liquid
15 compositions. Both halogen and peroxygen type bleaches are encompassed by this invention.

Among the suitable halogen donor bleaches are heterocyclic N-bromo and N-chloro imides such as trichlorocyanuric, tribromocyanuric, dibromo and dichlorocyanuric acids, and salts thereof with water solubilizing cations such as potassium and sodium. An example of the hydrated dichlorocyanuric acid is Clearon® CDB56, a product manufactured by the Olin Corp.. Such bleaching agents may be employed in
20 admixtures comprising two or more distinct chlorine donors. An example of a commercial mixed system is one available from the Monsanto Chemical Company under the trademark designation "ACL-66" (ACL signifying "available chlorine" and the numerical designation "66", indicating the parts per pound of available chlorine) which comprises a mixture of potassium dichloroisocyanurate (4 parts) and trichloroisocyanurate acid (1 part).

25 Other N-bromo and N-chloro imides may also be used such as N-brominated and N-chlorinated succinimide, malonimide, phthalimide and naphthalimide. Other compounds include the hydantoins, such as 1, 3-dibromo and 1,3-dichloro-5,5-dimethylhydantoin, N-monochloro-C, C-dimethylhydantoin methylene bis-(N-bromo-C,C-dimethylhydantoin); 1,3-dibromo and 1,3-dichloro 5-methyl-5-n-amyldantoin, and the like. Further useful hypochlorite liberating agents comprise tribromomelamine and trichloromelamine.

30 Dry, particulate, water-soluble anhydrous inorganic salts are likewise suitable for use herein such as lithium, sodium or calcium hypochlorite and hypobromite.

Preferred chlorinating agents include potassium and sodium dichloroisocyanurate dihydrate, chlorinated trisodium phosphate and calcium hypochlorite. Particularly preferred are sodium or potassium dichloroisocyanurate dihydrate. Preferred concentrations of all of these materials should be such that they
35 provide about 0.2 to about 1.5% available chlorine. Hypochlorite liberating compounds may generally be employed in automatic dishwashing detergents at a level of from 0.5 to 5% by weight, preferably from 0.5 to 3%.

Suitable chlorine-releasing agents are also disclosed in the ACS monograph entitled "Chlorine - Its Manufacture, Properties and Uses" by Sconce, published by Reinhold in 1962.

40 Chlorine bleach sources of the present invention may be encapsulated by the processes disclosed in EP-A-0,510,761.

It may be appreciated that the oxygen bleaches which may be included in the compositions of the invention are alkali metal and ammonium salts of inorganic peroxygen compounds such as perborates, percarbonates, persulfates, dipersulfates and the like. Generally the inorganic oxygen compound will be
45 used in conjunction with an activator such as TAED (tetraacetyl ethylene diamine), sodium nonyl oxybenzene sulfonate or choline sulfophenyl carbonate or a catalyst such as manganese or other transition metal, as is well known in the bleaching art (see e.g., U.S. 5,041,232; 5,045,223; and 5,047,163, Batal et al. describing organic catalysts). Insoluble organic peroxides such as diperoxydodecanedioic acid (DPDA), phthalimidoperoxyacetic acid (PAP) or lauroyl peroxide, or benzoyl peroxide, may also be used. Many
50 others known in the art may also be used. Generally, the peroxygen compounds are present at a level of from 0.5 to 20% by weight, 0.005 to 5% catalyst and/or 0.5 to 3% activator.

Surfactants

55 If encapsulated chlorine bleach is used in the present invention, a wide variety of alkoxylates may be used. Particularly preferred are the defoaming nonionics such as those given in U.S. Patent No. 4,973,419.

It may also be appreciated that low-foaming bleach resistant surfactants may also be included in the liquid detergent formulas of the present invention, as are known in the art. The preferred range of a

surfactant useful in the invention is about 0.5 to about 4.0%.

Inorganic Builders

5 Inorganic builders in an amount of from about 3 to about 30%, preferably 3 to 10%, may also be present in the formula as water hardness sequestering agents or builders.

Use of the sequestrant, in excess of its solubility limit within the formula requires that the solid be present as fine particles which are suspended by the structuring system. The presence of solids will affect the viscosity of the liquid and may modify the range of the structurants needed to deliver the proper
10 rheology. Inorganic builders which may be used are sodium and potassium salts of polyphosphate, orthophosphate, carbonate, bicarbonate, sesquicarbonate and borate.

Water-insoluble aluminosilicate ion-exchange materials may be used as alternative builders (e.g. GB 1,473,201 and 1,473,202 - Henkel). These are crystalline or amorphous materials of general formula

15 $(\text{Cat}_{2n}\text{O})_x \cdot \text{Al}_2\text{O}_3(\text{SiO}_2)_y \cdot z\text{H}_2\text{O}$

wherein Cat is a cation having a valency n that is exchangeable with Calcium (e.g. Na^+ or K^+); x is a number from 0.7 to 1.5; y is a number from 1.3-4; and z is such that the bound water content is from 1% to 28% by weight. Preferred is the commercially available product Zeolite type A.

20 $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}$

Silicates

25 Of the alkaline metal silicates, sodium silicate having a ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of from about 1.0 to about 3.3, preferably from about 2 to about 3.2 is useful for the present invention. The liquid silicate form is preferred. Solid silicates may also be used either alone or in combination with liquid silicates.

Thickeners and Stabilizers

30 Thickeners for use in the compositions according to the invention are disclosed in U.S. Patent No. 4,836,948 (Corring) herein incorporated by reference. Particularly preferred thickeners are the cross-linked polymers having molecular weights ranging from about 500,000 to about ten million, preferably between 500,000 and 4,000,000. Examples of commercially available cross linked polymers are the Carbopol® resins
35 manufactured by the B.F. Goodrich Chemical Company. These materials include Carbopol 941® (m.w. 1,250,000) Carbopol 934® (m.w. 3,000,000), Carbopol 940® (m.w. 4,000,000) and Carbopol 617® (m.w. 4,000,000). Analogs provided by other manufacturers would also be useful. The chlorine bleach may be encapsulated, thus polymers such as those disclosed in U.S. Patent No. 4,260,528 (Fox et al.) may also be used.

40 The thickening polymer is present in the compositions in a range of 0 to about 3.0 by wt./ and preferably about 0.4% to about 1.5% by wt.

Co-structurants or stabilizers may also be used in combination with the thickeners. Examples of such preferred co-structurants and stabilizers include (1) alumina described in U.S. Patent No. 4,836,948, (2) alkali metal silico aluminate described in U.S. Patent No. 4,941,988, (3) polyvalent metal soaps, described in
45 U.S. Patent No. 4,752,409 and (4) a synthetic hectorite clay such as Laponite® XLS supplied by Waverly Mineral Products Co., subsidiary of Laporte, Inc..

Preferred co-structurants include alumina and the hectorite clays. The co-structurants may be used in a range of from about .005 to 1%; preferably about .01 to about .5%; and especially preferred about .01 to about .1%.

Scale Inhibitors and Anti-Scalants

55 An anti-scalant agent inhibits the development of the microscopic nuclei to the critical size and then the agent redisperses to act on other nuclei. Anti-scalant agents are also useful in broader applications such as in industrial boilers, water purification, evaporators, etc.

Any conventional anti-scalant (sometimes described as dispersant) which is used to prevent the deposition of sparingly soluble salt scale, such as CaCO_3 in water systems is considered within the scope of this invention.

Anti-scalant agents are available in either powder or solution form, generally solution form is available, and may be provided as acids, partially neutralized acids or otherwise contain a free acid. Examples of suitable phosphorus containing scale inhibitors include methylene phosphonates, methylene phosphonic acid, and other phosphates and phosphonates listed in McCutcheon's Functional Materials, North America Edition, Volume 2, McCutcheon Division Publishing, Glen Rock, New Jersey (1991).

Preferred methylene phosphonates include pentasodium amino tris, hexamethylene diamine tetra, hexapotassium, octasodium diethylene triamine penta.

Particularly preferred methylene phosphonic acids include diethylene triamine penta acid. Especially preferred is hydroxy ethylene diphosphonic acid in aqueous solution supplied as Arquest® 710 by Aquaness Chemicals or as Dequest® 2010 by Monsanto. The same diphosphonic acid is available in powder form as Dequest® 2016D by Monsanto or amino tri (methylene phosphonic acid) sold as Arquest® 709 by Aquaness Chemicals. Polymeric anti-scalants suitable for the invention include polymaleic acid and its sodium salts (Belclene® 200 and 201) supplied by Ciba-Geigy a polycarboxylate polymer series prepared from the copolymerization of acrylic and maleic acid sold under the Sokalan® CP Series by BASF of and sodium polyacrylates and polyacrylic acid available under the Sokalan PA Series supplied by BASF.

A polyacrylic acid and a sodium or ammonium polyacrylate are also suitable, such as products produced by Alco Chemical Corp., Division of National Starch and Chemicals, known as the Alcosperse® Series, Colloids sold by Rhone-Poulenc Corp. Good-rite® Series supplied by B.F. Goodrich and Acusol® Series supplied by Rohm & Haas.

Particularly preferred anti-scalants include Colloid® 117/50; Colloid® 211, 223(D) and 274; Good-rite® K-732, K-752, K-7058, K-G00N; Acusol® 445, and Alcosperse® 602N.

Additional anti-scalants suitable for the invention are described in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Volume 7, John Wiley & Sons, NY (1979), describing anti-nucleation agents or anti-scalants as dispersant materials.

A sulfonated styrene maleic anhydride copolymer is also a suitable anti-scalant for the invention and may be obtained as Versa® TL 7 supplied by National Starch. Other copolymers include Narlex® D-82 supplied by National Starch and sodium lignosulfonates supplied under the trademark Orzans® by ITT Rayonier.

Optional Ingredients

Bleach stable colorants such as Direct Yellow 28 and others disclosed in GB patent application No. 2,233,662 allowed August 9, 1991 may be used in the present invention. Bleach sensitive dyes such as those described in U.S. Patent No. 4,464,281 may also be used in embodiments containing oxygen or encapsulated bleach. Alternatively, pigments such as Ultramarine Blue 5151 or Ultramarine Blue 17 may also be used. Greater latitude in the selection of perfume ingredients is provided because destabilization by chlorine is not a factor.

If additional defoaming is desired, silicones such as a polydimethyl siloxane with 6% hydrophobed silica supplied as Antifoam DB-100® by Dow Corning may be used. Minor amounts of other ingredients such as anti-tarnish agents, soil suspending agents, hydrotropes, etc. may also be included in the inventive formulations. The amount of each optional additive is no greater than about 0.5% by weight.

The following examples will serve to distinguish this invention from the prior art, and illustrate its embodiments more fully. Unless otherwise indicated, all parts, percentages and proportions referred to are by weight.

Example I

The hypochlorite stability of the sequestrants was measured. A standard thiosulfate titration for remaining hypochlorite was performed. pH 12 solutions containing 5% sequestant and hypochlorite bleach to deliver 1% AvCl_2 were prepared. The solutions were stored in a 40°C oven to accelerate bleach decomposition. Results are tabulated below. Structures are given in Table 2.

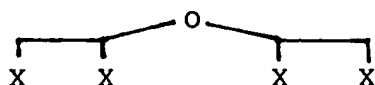
Table 1

Species	8-Day % AvCl ₂ at 40 ° C
Oxydisuccinate (ODS) ^I	96 (48% at 32 days)
Ethylene glycol disuccinates (EGDS) ^{II}	97
Propylene glycol disuccinate (PGDS) ^{III}	98

Table 2

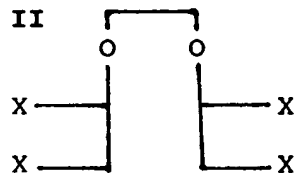
Generic Chemical Structures for the Species of Table 1 are as follows

I



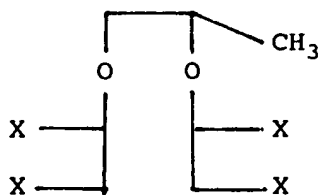
ODS

II



EGDS

III



PGDS

wherein X = COOH

It is noted from Tables 1 and 2 above, that none of the ether carboxylates (ODS, EGDS or PGDS) decompose the available chlorine of the sample solutions. However, only ODS is also biodegradable (see Example II).

Example II

The solutions of Example I were tested by the modified Semi-Continuous Activated Sludge (SCAS) test described above to determine the biodegradability of the selected ether carboxylate builders. Sludge samples containing each of the builders were placed in 1,500 ml aeration units and tested as described by the OECD guidelines. The acclimatization time for the builders resulting from the modified SCAS testing are given below:

Species	Modified SCAS Acclimatization Times	DOC Percentages
ODS	2-3 weeks	>80%
EGDS	7 weeks	>80%
PGDS	9 weeks	>80%

Examples III-VI

Compositions useful as liquid detergent compositions are listed below:
A composition including sodium tripolyphosphate as a builder is listed for comparison purposes.

Examples 3-6 ADL Formulas

Component	3	4	5	6
Sodium Disilicate (2.0 ratio)	15.0	15.0	15.0	15.0
Carbopol 940 ^a	1.2	1.2	1.2	1.2
CDB Wax Encapsulates (to give 1.0% AvCL)	3.6	3.6	3.6	3.6
SLF-18 ^b	2.0	2.0	2.0	2.0
Chlorine Donor (to give 1% AvCl)	--	--	--	--
Alcosperse 602N (AA) ^c	--	5.0	--	5.0
Sokalan CP-7 ^d (2:1 AA/MA)	--	--	5.0	--
STPP (Anhydrous)	25.0	--	--	--
ODS	--	10.0	--	--
EGDS	--	--	10.0	--
PGDS	--	--	--	10.0

All components are listed in terms of active percentages and builder molecules are presented as sodium salt levels.

- a) a 4,000,000 MW cross-linked polymer supplied by B.F. Goodrich Chemical Co.
- b) a low-foaming surfactant supplied by BASF.
- c) anti-scalant supplied by National Starch.
- d) copolymerization product of acrylic and maleic acid supplied by BASF.

Examples VII-X

One of the criteria used to judge the performance of a dishwasher detergent is glassware appearance after washing. In this example, ten glass tumblers were placed in a Sears Kenmore dishwasher. Forty grams of a 4:1 mixture of margarine and powdered milk were placed in the dishwasher. 40 grams of each of the formulas shown below were added to the dishwasher dispenser cups. After repeating the test through 4 wash cycles, glasses were visually inspected and rated. They were rated numerically for spotting and filming on a scale of 0 to 4 (0 = best; 4 = worst) for spotting, and 0 to 5 (0 = best; 5 = worst) for filming. Differences of about 0.5 in spotting, and 1.0 in filming are considered significant compared to a 25% liquid STPP formula. Lipstick soiled glasses were placed in the dishwasher as a builder sensitive monitor. Removal of fatty acids of pigments in lipstick formulations are sensitive to both builders and surfactant.

The results are as follows:

Example	Formula	Spotting	Filming	% Lipstick Remaining
7	10% ODS	0	1.4	Trace
8	10% PGDS	0	1.8	Trace
9	10% EGDS	0.2	2.0	Trace
10	25% STPP	0.3	0.9	Trace

ODS was observed to have significantly better overall performance in preventing spotting, filming and lipstick remaining on the dishware over both EGDS and STPP, the phosphate based composition. Although ODS and PGDS had almost parity performance, PGDS is not biodegradable according to the modified SCAS test.

Example XI

A liquid detergent composition including ODS may be prepared as described in Examples III-VI except the chlorine source used is 1% hypochlorite to provide 1% available chlorine and the surfactant, SLF-18, is omitted from the formula.

Claims

1. An automatic dishwashing detergent liquid composition comprising:
 - (a) about 3% to about 30% by weight of an ether carboxylate compound selected from the group of oxydisuccinates; the ether carboxylate being both hypochlorite resistant and biodegradable, as defined by the modified SCAS test.
 - (b) a chlorine donor providing about 0.2 to about 1.5% by weight of available chlorine;
 - (c) about 0.1 to about 6% by weight of a thickening agent; and
 - (d) about 3 to about 30% by weight of an inorganic builder.
2. The composition according to claim 1, wherein the oxydisuccinate is 2,2'-oxydisuccinate.
3. The composition according to claim 1, wherein the thickening agent is a polymer having a molecular weight of from about 500,000 to about 10,000,000.
4. The composition according to claim 1, wherein the inorganic builder is selected from the group consisting of alkaline metal silicates, alkaline metal carbonates, bicarbonates, sesquicarbonate, aluminosilicates and mixtures thereof.
5. The composition according to claim 4, wherein the inorganic builder is selected from the group of alkaline metal carbonates and alkaline metal bicarbonates.
6. The composition according to claim 1, further comprising about 0.5 to about 15% by weight of an anti-scalant agent.
7. The composition according to claim 7, wherein the anti-scalant is selected from the group of phosphonates, polyacrylic acid and a sodium or ammonium polyacrylate.
8. The composition according to claim 1, further comprising about 0.5 to about 4% by weight of a low foaming surfactant.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3868

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y	US-A-4 105 573 (R.L. JACOBSEN) * the whole document *	1-8	C11D3/395 C11D3/20
D,Y	US-A-4 933 101 (W.A. CILLEY ET AL.) * the whole document *	1-8	
D,Y	EP-A-0 385 595 (THE PROCTER & GAMBLE CO.) * the whole document *	1-8	
D,A	EP-A-0 192 441 (THE PROCTER & GAMBLE CO.) * claims; examples III,IV *	1,2	
A	EP-A-0 367 296 (THE PROCTER & GAMBLE CO.) * page 8, line 5 - line 16 * * page 10, line 41 - page 12, line 3 * * page 13, line 27 - line 57; claims *	1,2,4-8	
A	DE-A-2 304 404 (MONSANTO CO.) * claims *	1,8	
A	US-A-4 182 684 (K.P. LANNERT) * claims *	1,8	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 MARCH 1993	Examiner SERBETSOGLU A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document			

